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ICHIDA MASANORI****(54) ELECTROLYTIC MANGANESE DIOXIDE POWDER, AND MANUFACTURING METHOD THEREOF**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrolytic manganese dioxide powder having a large specific surface area, together with its manufacturing method, which is used as a positive electrode active material for an alkali manganese battery.

SOLUTION: The electrolytic manganese dioxide powder has a maximum particle size of 100 μ m or less while the number of particles whose diameter is 1 μ m or larger is less than 15%, with its median size being 20-60 μ m. A specific surface area is 50 m²/g or larger when measured by a mixed gas adsorption process of nitrogen and helium after the powder is deaerated in the nitrogen at 150°C.

JAPANESE

[JP,2002-289185,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]In a diameter of grain of maximum size, the number of a particle (100 micrometers or less and 1 micrometer or less) at less than 15%. And electrolytic manganese dioxide powder after the median size's being the electrolytic manganese dioxide powder in the not less than 20-micrometer range of 60 micrometers or less and deaerating this powder at 150 ** among nitrogen, wherein specific surface area measured with a mixed gas adsorption process of nitrogen and helium is more than 50-m²/g.

[Claim 2]Electrolytic manganese dioxide powder which is the electrolytic manganese dioxide powder according to claim 1, and has the powder compact density rho at the time of fabricating this powder 5g by the pressure P to discoid 2 cm in diameter in the range of the following expressions of

relations (1).

$\rho \propto (0.2 \times P + 2.5)$ (1)

(Powder compact density (g/cm^3) and P are the pressures at the time of producing a powder compact (ton/cm^2), and ρ is $1 \leq P \leq 3$ here.)

[Claim 3] Face manufacturing electrolytic manganese dioxide powder and concentration of divalent manganese uses as an electrolysis solution solution of manganese sulfate and sulfuric acid whose temperature concentration of $60 \text{ g/l} - 80 \text{ g/l}$, and sulfuric acid is $20 \text{ g/l} - 60 \text{ g/l}$, and is not less than 90°C . Within a cell provided with the anode and the negative pole, it electrolyzes by electrolytic current density of the range of two or more 50 A/m^2 . A manufacturing method of the electrolytic manganese dioxide powder according to claim 1 to 2 characterized by classifying after grinding massive electrolytic manganese dioxide produced on the anode by exfoliating the electrolytic manganese dioxide sludge which carried out electrocrystallization adherence.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the electrolytic manganese dioxide powder which has the shape of specificity of electrolytic manganese dioxide used as positive active material, and its manufacturing method, for example in a manganese dry battery, especially an alkaline manganese battery.

[0002]

[Description of the Prior Art]Electrolytic manganese dioxide powder is known, for example as positive active material of a manganese dry battery or an alkaline manganese battery.

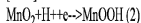
It excels in preservability and has the advantage of being cheap.

[0003]Since especially the alkaline manganese battery using electrolytic manganese dioxide powder as positive active material is excellent in the discharge characteristic in heavy loading, it is broadly used even for an electronic camera, a portable tape recorder, a portable information device and also a game machine, or a toy, and the demand is being extended to urgency in recent years. However, an alkaline manganese battery has the technical problem that service capacity is spoiled greatly, in order for the quantity for which the electrolytic manganese dioxide powder which is positive active material is used to fall and for discharge voltage to fall as discharge current becomes large. Electrolytic

manganese dioxide which is the positive active material with which it fills up if an alkaline manganese battery is used for the apparatus which in other words uses a high current is not fully used, but it has the fault that a hour of use becomes short.

[0004]The discharge reaction of electrolytic manganese dioxide (MnO_2) in an alkaline dry cell is discharged with the following reaction formulae (2).

[0005]



(2) Electrolytic manganese dioxide advances, consuming H^+ (proton) supplied from the water in the alkaline aqueous solution which is an electrolysis solution so that clearly from a formula. That is, on the occasion of the discharge reaction of electrolytic manganese dioxide, supply of water is indispensable and electrolytic manganese dioxide needs to carry out H^+ and a reaction promptly.

[0006]The most effective solving means of the technical problem said that the utilization efficiency of electrolytic manganese dioxide in the alkaline dry cell used for the apparatus used by a high current from this falls. In order to have large specific surface area in order to make the utilization efficiency of electrolytic manganese dioxide with which it fills up in the cell increase, and to secure sufficient reaction surface product with H^+ (proton), the specific surface area in which especially the electrolytic manganese dioxide powder of a large-current-discharging alkaline manganese battery use is large enough is required. However, the specific surface area of the conventional electrolytic manganese dioxide powder was at most $40\text{-m}^2/\text{g}$, and it was difficult to acquire sufficient utilization efficiency in large current discharging.

[0007]Furthermore, when especially electrolytic manganese dioxide powder is used as positive active material of an alkaline manganese battery, let it be a cell anode as a powder compact which carried out pressing of the electrolytic manganese dioxide powder to discoid or ring shape.

[0008]Therefore, in order to supply an electrolysis solution to the powder compact depths promptly according to advance of a discharge reaction, it was thought that the one where specific surface area is large and where powder molding density is lower was desirable.

[0009]

[Problem(s) to be Solved by the Invention]Especially this invention aims to let the electrolytic manganese dioxide powder used as positive active material of an alkaline manganese battery provide the electrolytic manganese dioxide powder which has large specific surface area, and its manufacturing method.

[0010]

[Means for Solving the Problem]This invention persons came to complete an invention of electrolytic manganese dioxide powder which has large specific surface area, as a result of repeating examination wholeheartedly. If in charge of manufacturing this electrolytic manganese dioxide powder, as a result of examining an electrolytic condition of electrolysis temperature and electrolysis solution concentration in an electrolysis process of electrolytic manganese dioxide, it came to complete that manufacturing method.

[0011]Namely, electrolytic manganese dioxide powder of this invention, In a diameter of grain of maximum size, the number of a particle (100 micrometers or less and 1 micrometer or less) at less than 15%. And it is the electrolytic manganese dioxide powder which has the median size in the not less than 20-micrometer range of 60 micrometers or less, After deaerating this powder at 150 ** among nitrogen, it is electrolytic manganese dioxide powder, wherein

specific surface area measured with a mixed gas adsorption process of nitrogen and helium is more than 50-m²/g. [0012]It is the electrolytic manganese dioxide powder which has the powder compact density rho at the time of carrying out pressing of the 5 g to discoid 2 cm in diameter in the range of the following expressions of relations (1) in this powder.

[0013]

$$\rho < (0.2xP + 2.5) \quad (1)$$

(Powder compact density (g/cm³) and P are the pressures at the time of producing a powder compact (ton/cm²), and rho is 1 <= rho <= 3 here.)

A manufacturing method of electrolytic manganese dioxide powder, Within a cell with which concentration of divalent manganese was provided with the anode and the negative pole by using as an electrolysis solution solution of manganese sulfate and sulfuric acid whose temperature concentration of 60 g/l - 80 g/l, and sulfuric acid is 20 g/l - 60 g/l, and is not less than 90 **, After electrolytic current density grinds massive electrolytic manganese dioxide produced by exfoliating the electrolytic manganese dioxide sludge which electrolyzed in the two or more 50 A/m range, and carried out electrocrystallization adherence on the anode, it is because it classifies.

[0014]Hereafter, it explains still in detail about this invention.

[0015]When especially electrolytic manganese dioxide powder is used as positive active material of an alkaline manganese battery, in order to give conductivity to electrolytic manganese dioxide powder, let it be a cell anode as a powder compact which carried out pressing of the powder mixture which added carbon etc. to discoid or ring shape. It inserts in the iron battery cans which gave cylindrical nickel plating which constitutes a cell for this further, and a cell is constituted.

[0016]In this invention, having defined a diameter of grain of maximum size of electrolytic manganese dioxide powder, the number of a particle of 1 micrometer or less, and a median size is based on a reason explained below.

[0017]That is, in electrolytic manganese dioxide powder obtained by this invention, if powder of size over 100 micrometers exists, as a result of damaging inside of a battery can, it reacts to iron which damaged plating given to a battery can and was exposed, and becomes causes, such as the generation of gas. A powder compact which carries out pressing of zinc which furthermore serves as a cell negative electrode, and the electrolytic manganese dioxide powder used as a cell anode, Breakage of a separator for insulating electrically is caused, and direct contact will be carried out, and during preservation of a cell, electrolytic manganese dioxide powder which is positive active material, and zinc which is cell negative electrodes produce self-discharge, and causes capacity lowering.

[0018]Quantity of electrolytic manganese dioxide which it becomes insufficient [a particle of 1 micrometer or less] contacting carbon for giving conductivity, and the number can use at not less than 15% will be spoiled greatly.

[0019]The total surface area of electrolytic manganese dioxide powder falls, and, as for that in which a median size exceeds 60 micrometers, reactivity worsens. Furthermore, restoration nature is greatly spoiled for a median size electrolytic manganese dioxide powder below 20 micrometers.

[0020]By the above reason, a median size requires that a diameter of grain of maximum size of electrolytic manganese dioxide powder of this invention should be less than 15%, and the number of a particle (100 micrometers or less and 1 micrometer or less) should be not less than 20 micrometers 60 micrometers or less.

[0021]As stated above, in electrolytic manganese dioxide powder of this invention, the number of a diameter of grain of maximum size and a particle of 1 micrometer or less and also regulation of a median size are important. About a

particle size of electrolytic manganese dioxide powder of this invention, it measured by a method described below.
 [0022](A diameter of grain of maximum size, the number of a particle of 1 micrometer or less, measuring method of a median size) A solution which carried out dispersed suspension of the electrolytic manganese dioxide powder manufactured with a manufacturing method of this invention is irradiated with a laser beam, Measurement of particle diameter of electrolytic manganese dioxide powder and the number was performed using light scattering measurement (the Nikkiso [Co., Ltd.] make, a trade name: micro track) measured by the scattered light. In this method, particle diameter of electrolytic manganese dioxide powder which carried out dispersed suspension was measured, and the number and a median size of a diameter of grain of maximum size of electrolytic manganese dioxide and a particle of 1 micrometer or less were measured.

[0023]As mentioned above, large specific surface area of electrolytic manganese dioxide powder is especially required for an alkaline manganese battery for high currents. Electrolytic manganese dioxide powder of this invention is provided with large specific surface area, and checked it by a method of measuring specific surface area of electrolytic manganese dioxide powder of this invention described below. The powder compact density ρ was measured.

[0024](Measuring method of powder specific surface area) It is a deed about 40-minute indirect desulfurization mind at 150 °C among a nitrogen air current of a flow of flow after extracting 0.3g of electrolytic manganese dioxide powder manufactured with manufacturing method of this invention and putting it into measuring pipe made from Pyrex tube 20 cc/min.

[0025]Specific surface area of electrolytic manganese dioxide powder was measured using a method (the Shibata science machine-industry company make, a trade name: automatic surface area measuring device ASA-2000 type) of immersing a measuring pipe into liquid nitrogen and measuring the amount of adsorption gas, flowing nitrogen-helium mixed gas promptly after an end of deaeration.

[0026](Measuring method of the powder compact density ρ) 5g of electrolytic manganese dioxide powder manufactured with a manufacturing method of this invention is extracted, Put into a cylindrical metallic mold 2 cm in diameter, and thickness of each powder compact which might be pressurized by a pressure of 1 ton/cm² or 3 ton/cm² from a sliding direction is measured, Furthermore, powder compact volume was computed from a diameter of a disc-like powder compact, and it measured by a method of calculating the powder compact density ρ from volume and weight of a powder compact.

[0027]If it is in electrolytic manganese dioxide powder of this invention, A result of having created a disc-like powder compact with compacting pressure from which 1 ton/cm² or 3 ton/cm² differs, and having searched for the powder compact ρ , In compacting pressure of 1 ton/cm², the powder compact density ρ has the thing powder compact density ρ smaller than 2.7 g/cm³. In compacting pressure of 3 ton/cm², the powder compact density ρ has the thing powder compact density ρ smaller than 3.1 g/cm³, and is the electrolytic manganese dioxide powder in the range of an expression of relations (1) shown below.

[0028]
 $\rho < (0.2P + 2.5) \quad (1)$

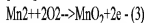
(Powder compact density (g/cm³) and P are the pressures at the time of producing a powder compact (ton/cm²), and ρ is $1 < \rho < 3$ here.)

In a manufacturing method of this invention, concentration of divalent manganese (Mn²⁺) uses as an electrolysis solution solution of manganese sulfate and sulfuric acid whose temperature concentration of 60 g/l - 80 g/l, and

sulfuric acid is 20 g/l - 60 g/l, and is not less than 90 **, Within a cell provided with the anode and the negative pole, electrolytic current density electrolyzes in the range more than 80 A/m², and after grinding massive electrolytic manganese dioxide produced by exfoliating the electrolytic manganese dioxide sludge which carried out electrocrystallization adherence on the anode, electrolytic manganese dioxide powder is manufactured by classifying. This is based on a reason explained below.

[0029]Electrolytic manganese dioxide deposits on the anode by electrolysis according to the following reaction formulae (3).

[0030]



For this reason, when there is little Mn²⁺ concentration in an electrolysis solution as less than 40 g/l and sulfuric acid concentration exceeds 60 g/l, as a result of Mn²⁺ short supply to an anode top occurring, a rise of electrolytic voltage is caused, oxygen evolution is caused on the anode, and efficiency falls.

[0031]In being higher than Mn²⁺ concentration of 80 g/l, beta-MnO₂ from which structure differs in electrolytic manganese dioxide generates.

[0032]In sulfuric acid concentration, from 20 g/l, when Mn²⁺ concentration is low still lower than 20 g/l, beta-MnO₂

with low alkali potential generates in electrolytic manganese dioxide. When still higher than sulfuric acid concentration of 60 g/l, a rise of electrolytic voltage is caused, oxygen evolution is caused on the anode, and efficiency falls.

[0033]Although electrolysis generation in a range still wider than electrolysis solution concentration in this invention is possible for electrolytic manganese dioxide, In order for large specific surface area of this invention to also obtain ***** , it is necessary to specify Mn²⁺ concentration and sulfuric acid concentration in an electrolysis solution, and concentration of divalent manganese (Mn²⁺) is [concentration of 60 g/l - 80 g/l, and sulfuric acid of the range] 20 g/l - 60 g/l.

[0034]It is indispensable to perform electrolysis temperature in a manufacturing method of this invention above 90 **, and to perform electrolytic current density above 50 A/m². This is because specific surface area of electrolytic manganese dioxide powder is insufficient and the purpose of this invention cannot be attained, when electrolysis temperature is less than 90 ** and electrolytic current density is less than 80 A/m².

[0035]In a manufacturing method of this invention, although a positive plate in electrolytic production of electrolytic manganese dioxide uses titanium, it cannot be overemphasized that it is applicable even if it is other titanium alloys, a lead plate, and a black lead board. Since electrolytic manganese dioxide which deposited on an electrode exfoliates by a shock, its shock-proof outstanding titanium or titanium alloy is more desirable.

[0036]One side grinds a grinding method in a manufacturing method of this invention to 3 to 5-cm mass material with a jaw crusher as coarse grinding, and in order to perform pulverizing further, it grinds with a roll crusher. A mortar ground further after that. Furthermore, dry type ball milling was also used together if needed.

[0037]In this grinding, grinding in a JAI rate crusher etc. is also possible in addition to a jaw crusher of coarse grinding. everything but grinding furthermore according to a mortar -- wet ball mill grinding and a mortar (mill) -- it cannot be overemphasized that grinding etc. can be applied. Since impalpable powder is further removable by distributing further electrolytic manganese dioxide powder which it was based on a sieve in a classification method,

and also was ground and obtained in pure water, filtering sedimentation powder, and drying in a 70 °C air current, it is more desirable. If it restricts to especially an alkaline manganese battery use, Although electrolytic manganese dioxide powder is further neutralized in Na_2CO_3 or a NaOH aqueous solution and rinsing and desiccation are performed, even if it is a case where such operation is performed, this invention can be applied and it is not limited to these.

[0038]

[Example]An example and a comparative example explain this invention in detail below.

[0039]You made it hang so that it may face each other in a titanium plate as the anode and a cell with a content volume of 20 l. which formed the heating device may be faced in a black lead board as the negative pole when manufacturing example 1 electrolytic manganese dioxide, respectively, and what formed the pipe for supplying a manganese sulfate solution from the cell upper part was used.

[0040]Pouring this solution into said cell using a manganese sulfate solution as electrolysis supply liquid. It faced electrolyzing, it adjusted so that the presentation of the electrolysis solution under electrolysis might serve as divalent manganese concentration of 70 g/l, and sulfuric acid concentration of 50 g/l, and the temperature of the cell was kept at 95 °C, and it carried out by current density 100 A/m².

[0041]After electrolyzing for ten days, take out the anode titanium plate which electrolytic manganese dioxide electrodeposited, and with pure water After washing, Electrolytic manganese dioxide which carried out deposit adherence is exfoliated by blow on an anode titanium plate, After carrying out coarse grinding of the obtained mass material with the jaw crusher, the roll mill grinder's grinding finely further and a mortar's grinding after that, it classified with the sieve of 200 meshes of openings, and electrolytic manganese dioxide powder was obtained.

[0042]Thus, the particle size of the obtained electrolytic manganese dioxide powder, As a result of measuring using the light scattering measurement (the Nikkiso [Co., Ltd.] make, a trade name: micro track) which are suspended in powder by using a solvent as pure water, and irradiate there with a laser beam, the diameter of grain of maximum size was 90 micrometers, the number of a particle of 1 micrometer or less was 9%, and the median size was 52 micrometers.

[0043]After extracting this electrolytic manganese dioxide powder 0.3g and putting into the measuring pipe made from the Pyrex tube, Indirect desulfurization mind is performed at 150 °C among the nitrogen air current of the flow of flow 20 cc/min for 40 minutes, the method (the Shibata science machine industry company make.) of immersing a measuring pipe into liquid nitrogen and measuring the amount of adsorption gas, while flowing nitrogen-helium mixed gas promptly after the end of deaeration Trade name: As a result of measuring the specific surface area of electrolytic manganese dioxide powder using automatic surface area measuring device ASA-2000 type, specific surface area was 68m²/g.

[0044]5g of this electrolytic manganese dioxide powder was extracted, it put into a cylindrical mold 2 cm in diameter, the thickness of the powder compact which was 1-ton/cm²-pressurized and was fabricated from the upper and lower sides was measured, and the powder compact density rho fabricated by moulding pressure 1 ton/cm² was computed. These 5g of powder was extracted independently, and the powder compact density rho which put into a cylindrical mold 2 cm in diameter, measured the thickness of the powder compact which was 3-ton/cm²-pressurized and was fabricated from the upper and lower sides, and was fabricated by moulding pressure 3 ton/cm² was computed.

[0045]The powder compact density rho of this electrolytic manganese dioxide powder was 2.96 g/cm³, when the compacting pressure P was 1 ton/cm² and it was 2.62 g/cm³ and 3 ton/cm².

[0046]The measurement result of these electrolytic manganese dioxide manufacturing conditions, the diameter of grain of maximum size, the number of a particle of 1 micrometer or less, a median size, specific surface area, and powder compact density is shown in Table 1. In the following Examples 2-9 and comparative examples 1-3, the electrolytic manganese dioxide manufacturing conditions and a measurement result are similarly shown in Table 1.

[0047]The electrolytic condition shown in the Example 2 - example 4 table 1 was adopted, and electrolytic manganese dioxide was manufactured by the same method as Example 1. A measurement result is shown in Table 1.

[0048]Except example 52 value manganese concentration having been 60 g/l, and having made [sulfuric acid concentration] 90 ** and electrolytic current density into 60 A/m² for 60 g/l and electrolysis temperature, it carried out by the same method as Example 1, and deed electrolytic manganese dioxide powder was further obtained for the dry grinding by a ball mill for 12 hours. The result is shown in Table 1.

[0049]The electrolytic condition shown in the six to example 9 table 1 was adopted, and electrolytic manganese dioxide was manufactured by the same method as Example 5. A measurement result is shown in Table 1.

[0050]By the electrolytic condition shown in the comparative example 1 table 1, it carried out by the same method as Example 1, and deed electrolytic manganese dioxide powder was further obtained for the dry grinding by a ball mill for 12 hours. The result is shown in Table 1.

[0051]By the electrolytic condition shown in the comparative example 2 table 1, electrolytic manganese dioxide powder was obtained by the same method as Example 1. The result is shown in Table 1.

[0052]By the electrolytic condition shown in the comparative example 3 table 1, it carried out by the same method as Example 1, and deed electrolytic manganese dioxide powder was further obtained for the dry grinding by a ball mill for 24 hours. The result is shown in Table 1.

[0053]

[Table 1]

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The electrolytic manganese dioxide powder produced in Examples 1 thru/or 9 so that clearly from Table 1 all, The number of a particle (100 micrometers or less and 1 micrometer or less) is less than 15%, a median size is not less than 20 micrometers 60 micrometers or less, and, as for the specific surface area, in all, the diameter of grain of maximum size exceeds $50\text{-m}^2/\text{g}$. It turns out that the powder compact density ρ at the time of fabricating by 1 ton/cm^2 and 3 ton/cm^2 is in the range of the expression of relations (1) shown below altogether.

[0054]

$$\rho \leq (0.2xP + 2.5) \quad (1)$$

(Powder compact density (g/cm^3) and P are the pressures at the time of producing a powder compact (ton/cm^2), and ρ is $1 \leq P \leq 3$ here.)

On the other hand, although the diameter of grain of maximum size of each electrolytic manganese dioxide powder produced in the comparative examples 1 thru/or 3 is 100 micrometers or less, the number of a particle of 1 micrometer or less of the comparative example 1 is 21%.

A median size is 15 micrometers, and each specific surface area is less than $50\text{-m}^2/\text{g}$, and that of the comparative

example 3 is smaller than the specific surface area of this invention.

As for the specific surface area of the electrolytic manganese dioxide powder of this invention, what has high electrolytic current density is large, and it is desirable to be more desirably produced by the electrolytic current density in 80 A/m².

[0055]

[Effect of the Invention]As explained above, the electrolytic manganese dioxide powder obtained by the electrolytic manganese dioxide powder by this invention, and its manufacturing method, It is the remarkable and characteristic electrolytic manganese dioxide powder which has and carries out large specific surface area which is not in the former, and can expect to improve remarkably the high current service capacity of an alkaline manganese battery by using especially for an alkaline manganese battery. The manufacturing method can be excellent in economical efficiency, and can improve productivity remarkably.

[Translation done.]